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IDENTIFICATION OF SOURCES OF CHLORINATED DIOXINS AND FURANS IN FROG CREEK USING INTRODUCED MUSSELS (ELLIPTIO COMPLANATA)

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A. Hayton[1], D. Hollinger[2] and J. Martherus[1]

1. Water Resources Branch
Ontario Ministry of the Environment
125 Resources Road, P.O. Box 213
Rexdale, Ontario M9W 5L1

2. Water Resources Assessment Unit
Technical Support Section
Northwestern Region

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EXECUTIVE SUMMARY

In 1986, an in-depth study conducted to evaluate the water quality in the Rainy River found dioxins, including 2,3,7,8-tetraCDD in mussels exposed at the mouth of Frog Creek, a small tributary of Rainy Lake. Based on the congener distribution pattern of dioxins in the mussels it was suspected that the source was one or more of the wood waste disposal sites located in the watershed. In 1989, a follow-up study was conducted to identify the source(s).

The "Ski-Hill" wood waste disposal site was identified as the major source of dioxins and furans to Frog Creek. The dioxins and furans which had been found previously in the Fort Frances mill's lagoon sludge were likely being mobilized through erosion at the wood waste disposal site and appear to be entering Frog Creek via a drainage ditch. This conclusion was based on the known properties of dioxins and furans and the observation that wood waste was being eroded from the site.

The Miscampbell wood waste disposal site was identified as a minor source of the dioxin 2,3,7,8-tetraCDD through the Gun Club Creek to Frog Creek. Low levels of dioxins were also found in an agricultural drain but the source could not be identified.

INTRODUCTION

Studies by the Ontario Ministry of the Environment (OMOE) and the United States Environmental Protection Agency (USEPA) found polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs) in fish from the Rainy River and downstream in the Lake of the Woods (OMOE 1985, 1986; USEPA 1987). PCDDs were also found in the sludge and the suspended sediment of the effluent of the two Kraft pulp and paper mills on the river at Fort Frances on the Canadian side and International Falls on the American side (USEPA 1988; Clement *et al.* 1989).

In a subsequent study of the Rainy River by OMOE (1990), it was demonstrated that the mussel *Elliptio complanata* from an uncontaminated site could be used to detect PCDDs at a contaminated site after a short exposure period. The study also indicated that, in addition to the pulp and paper mill discharges on the Rainy River, there was a source of PCDDs to Frog Creek, a small tributary of Rainy Lake. Since the congener distribution pattern found in mussels from Frog Creek was similar to that found below the pulp and paper mills, it was suspected that the PCDDs originated from a pulp and paper mill operation.

In 1989, we undertook a study of Frog Creek to locate the source(s) of PCDDs in the watershed. The study design was based on the hypothesis that one or more of the three wood waste disposal sites in the Frog Creek watershed was the source. As in the previous study, the mussel *E. complanata* was used as a biomonitoring organism.

METHODOLOGY

Study Area

Our study area encompassed the 4 km of Frog Creek immediately upstream of Stanjikoming Bay of Rainy Lake (Figure 1). In the study area, the creek is slow-moving, averaging about 15 m in width and 1-3 m in depth. The shorelines in most areas are lined with emergent aquatic vegetation. In the study area there are three tributaries entering Frog Creek; the first, about 3 km from the mouth, drains the Ski-Hill wood waste disposal site; the second, about 2 km from the mouth, drains the area surrounding the Miscampbell wood waste disposal site; and the third, about 1.5 km from the mouth drains an agricultural area. A third wood waste disposal site that will be referred to as the New Site is located to the west of the Ski-Hill site.

Ski-Hill Site

This site was used as a municipal landfill from 1944 to 1979 and as a wood-waste disposal site between 1979 and 1988. About 100,000 m^3 of municipal waste and 900,000 m^3 of wood waste material, consisting of 74% bark, 12% paper mill and woodroom clarifier sludge, 10% settling pond sludge and 4% grit, lime and dregs were deposited at the site. On closure, the site was contoured and a 60 cm thick layer of clay was placed on the crown and a 30 cm thick layer of silt/clay was placed on the side slopes to reduce surface infiltration. Perimeter ditches were constructed to direct runoff away from the closed site and into the "Ski-Hill" drainage ditch (Figure 2). An inspection of this site at the time of the study

Fig.1. FROG CREEK STUDY AREA LOCATION

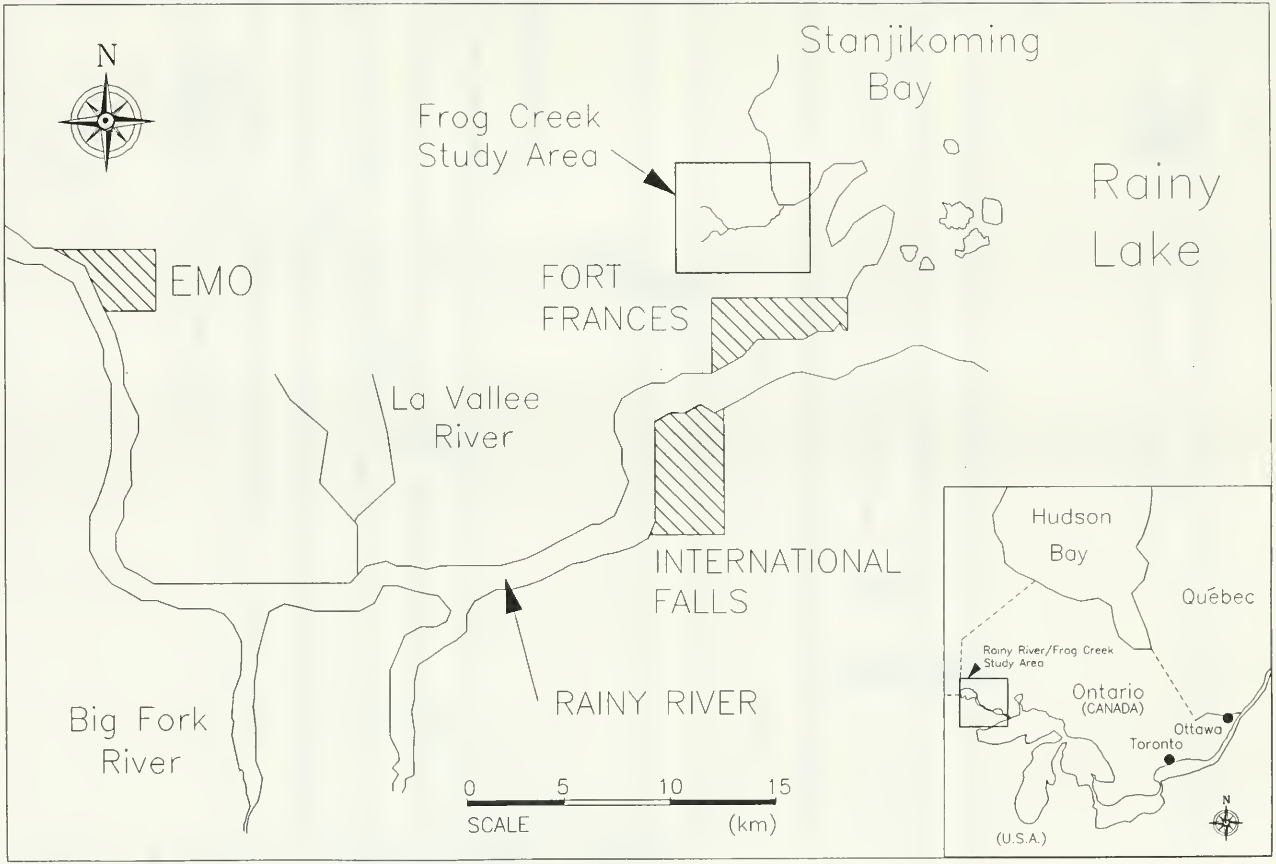
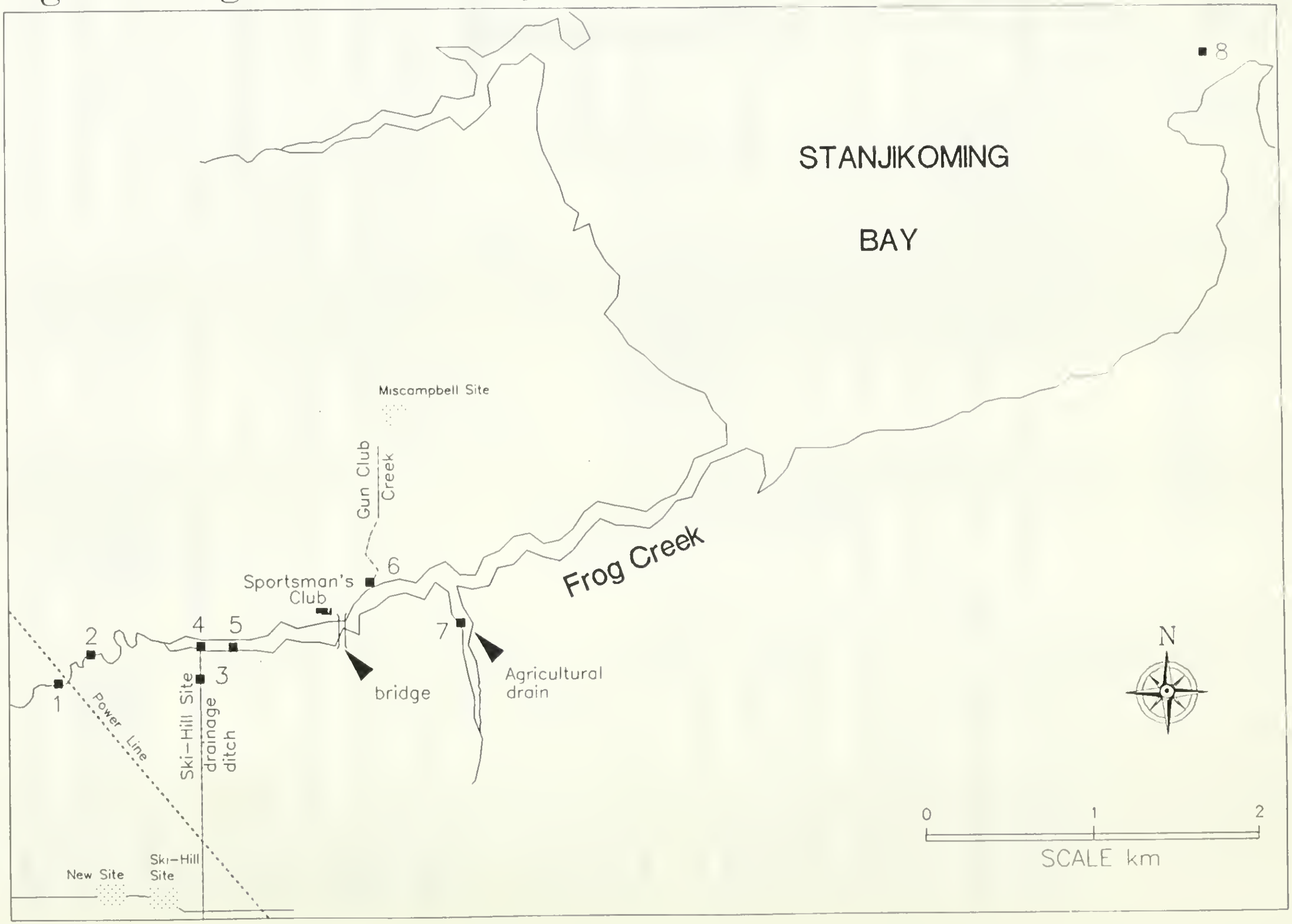


Fig.2. Frog Creek Study Area



indicated that some of the clay and silt-clay cover material had eroded, exposing wood waste. In addition, the cover material had not been vegetated.

New Site

This site was established in 1988 and will be in operation for many years. It has a total area of 75 hectares with a fill area of 15.5 hectares. Total waste deposited from 1988 to the end of 1989 was 20,500 m^3 and consisted exclusively of wood waste. Waste composition is essentially the same as at the Ski-Hill site; however, it is expected that the proportion of bark will be reduced in the future. Discharge from this site is directed to the west into a large, poorly drained area which drains into Frog Creek upstream of station 1. There is no creek or drainage ditch which would short circuit leachate from the site into Frog Creek.

Miscampbell Site

This site was used from 1974 to 1985 and was used for the disposal of wood waste only. A total of 225,000 m^3 of material was deposited with approximately the same breakdown of materials as the Ski-Hill Site. On closure the site was contoured and a 90 cm thick clay cap was placed over the surface of the site and a grass legume cover mixture was established. The leachate collection ditches were left in place. During wet periods, discharge from the site enters Frog Creek via the Gun Club Creek.

Field Methods

Eight stations were selected for study (Figure 2). Stations 1 and 2 were upstream of the Ski-Hill and Miscampbell wood waste disposal sites and served as controls. Station 3 was in the Ski-Hill drainage ditch; station 4 was at the mouth of this ditch where there was some mixing with Frog Creek water and station 5 was in Frog Creek 200 m downstream of the drainage ditch from the Ski-Hill wood waste disposal site. Site 6 was in the drainage ditch from the Miscampbell wood waste disposal site; station 7 was in an agricultural drain; and station 8 in Stanjikoming Bay of Rainy Lake, approximately 5 km from the closest suspected source of PCDDs.

Mussels (*E. complanata*) with a maximum shell length of 65 to 72 mm were collected from Balsam Lake (Victoria County) on June 27, 1989 maintained in Balsam Lake water with aeration at room temperature in 22 L buckets lined with food-grade plastic inserts. Concentrations of organochlorine contaminants in these mussels are usually below the analytical detection limits (Kauss and Hamdy 1985).

On July 4, 1989, clams were placed in envelope-shaped cages 30 cm by 45 cm of 1.25 cm galvanized mesh poultry netting. At each of the 8 stations, a cage containing 5 mussels was placed on the substrate.

On July 25, 1989, after an exposure period of 21 days, the caged mussels were collected. The mussels were immediately shucked, wrapped individually in hexane-rinsed foil, frozen

on dry ice and shipped to the Ministry of the Environment (OMOE) Laboratory in Rexdale, Ontario. Mussel tissue was stored at -20°C prior to analysis.

Analytical Methods

The pre-weighed biota samples were spiked with a mixture of $^{13}C_{12}$-labeled dioxin and furan congeners. The samples were then digested overnight using hydrochloric acid extracted by liquid-liquid extraction with a hexane/benzene mixture. The extraction was repeated three times.

The sample extract was evaporated almost to dryness and cleaned up using a dual two-stage column cleanup. The first set of columns contained sulphuric acid/silica and alumina absorbents. The second set consisted of a column containing silver nitrate modified silica followed by an alumina column. The columns were eluted with a series of solvents and the final extract was eluted to 10 uL using dry nitrogen.

The final extract was analyzed using high resolution gas chromatography/triple quadrupole mass spectrometry (HRGC/MS/MS) in the reaction ion monitoring mode using a Finnigan TSQ 70 instrument.

RESULTS

PCDDs and PCDFs were less than the analytical detection limit in mussels exposed at the two control stations (1, 2) upstream of the wood waste disposal sites (Table 1, Figure 2), indicating that there were no major sources upstream of the Ski-Hill site.

At station 3 in the Ski-Hill site drainage ditch, PCDDs and PCDFs were less than the analytical detection limit in mussels. However, at the mouth of the drainage ditch (station 4) where there is some mixing with Frog Creek water, mussels accumulated 6.3 pg/g of tetraCDD, including 2.3 pg/g of 2,3,7,8-tetraCDD, 2.7 pg/g tetraCDF, 4.3 pg/g of pentaCDD, 2.3 pg/g of heptaCDD and 3.4 pg/g of octaCDD. At station 5, 200 m downstream of the ditch in Frog Creek the levels in mussels were lower. TetraCDD was found in mussels at 3.4 pg/g which included 0.9 pg/g 2,3,7,8-tetraCDD; all other congeners were less than the analytical detection limit. Since PCDDs were detected at the confluence of the drainage ditch and Frog Creek, but not upstream, PCDDs must have been present in the drainage ditch but were not taken up to detectable levels in mussels. An hypothesis to explain this result is presented in the discussion. It is based partially on the assumption that water quality in the drainage ditch was poor and stressful to mussels. There is little direct evidence for this assumption. It is based on the visible observation that the water was highly coloured and turbid and that much of it originated from the Ski-Hill site.

At station 6, in Gun Club creek which receives drainage from the Miscampbell Site, PCDDs

TABLE 1:Dioxin and Furan concentrations (in pg/g wet weight) in mussels exposed in Frog Creek

STATION		1	2	3	4	5	6	7	8
SAMPLE	BLANK	CONTROL 1	CONTROL 2	INSIDE DRAINAGE DITCH	DRAINAGE DITCH MOUTH	200 m DOWNSTREAM DRAINAGE DITCH	GUN CLUB CREEK	AGRICULT. DRAIN	STANJIKO. BAY
Weight(g)		10.1	8.3	14.0	13.3	8.4	3.2 *	13.5	7.8
TetraCDD	ND(1.3)	ND(4.0)	ND(1.7)	ND(0.9)	6.3 <5>	3.4 <3>	ND(2.7)	0.7 <1>	ND(1.2)
2,3,7,8 TetraCDD					2.3	0.8			
PentaCDD	ND(1.1)	ND(5.2)	ND(2.3)	ND(0.6)	4.3 <3>	ND(3.1)	ND(4.7)	ND(1.0)	ND(0.8)
HexaCDD	ND(2.7)	ND(4.0)	ND(3.9)	ND(1.4)	ND(2.1)	ND(3.4)	ND(4.0)	ND(1.3)	ND(2.8)
HeptaCDD	ND(3.7)	ND(5.2)	ND(2.8)	ND(3.0)	2.3 <2>	ND(5.3)	ND(8.1)	ND(1.3)	ND(4.2)
OctaCDD	ND(4.5)	ND(15.0)	ND(4.9)	ND(4.4)	3.4 <1>	ND(5.5)	ND(29.3)	ND(3.7)	ND(6.5)
TetraCDF	ND(0.6)	ND(3.6)	ND(2.5)	ND(3.5)	2.7 <1>	ND(3.4)	ND(5.1)	ND(0.9)	ND(2.4)
PentaCDF	ND(1.1)	ND(4.7)	ND(2.5)	ND(0.9)	ND(2.1)	ND(5.2)	ND(5.0)	ND(1.9)	ND(1.1)
HexaCDF	ND(2.2)	ND(4.1)	ND(2.3)	ND(0.7)	ND(1.4)	ND(3.8)	ND(3.2)	ND(0.9)	ND(1.9)
HeptaCDF	ND(5.1)	ND(8.1)	ND(5.2)	ND(3.5)	ND(2.1)	ND(5.9)	ND(5.4)	ND(2.9)	ND(8.1)
OctaCDF	ND(6.0)	ND(13.7)	ND(3.7)	ND(3.2)	ND(3.2)	ND(3.5)	ND(11.7)	ND(4.1)	ND(5.5)
PERCENT RECOVERY									
TCDD	73	51	44	59	41	67	62	49	66
PCDD	75	57	51	59	67	78	71	60	80
HxCDD	69	53	53	55	79	76	79	63	77
HpCDD	56	52	64	64	73	67	67	46	62
OCDD	78	61	87	87	101	105	96	57	78

Note: ND() = Less than the detection limit shown in brackets
<> = Number of isomers detected
* = Low sample weight : 1 clam

and PCDFs were less than the analytical detection limit. However, tetraCDD was present in the mussel tissue and, while the level could not be quantitatively determined, it was close to the analytical detection limit of 2.7 pg/g. This suggests that some tetraCDD was or is escaping from the Miscampbell site.

At station 7, in an agricultural drain, only tetraCDD was above the detection limit at 0.7 pg/g none of which was 2,3,7,8-TCDD.

At station 8 in Stanjikoming Bay, PCDD and PCDF levels were less than the analytical detection limit.

In the study undertaken in 1986 (OMOE 1990), PCDDs were found at a station at the mouth of Frog Creek. Mussels were exposed at the same location in this study; however, data are not available because of a laboratory accident.

DISCUSSION

Identification of Sources of PCDDs and PCDFs

The results of this study indicate that PCDDs and PCDFs are or have been escaping from the Ski-Hill wood waste disposal site and to a lesser extent the Miscampbell wood waste disposal sites. It is known that there are PCDDs and PCDFs at these sites because sludge from the Fort Frances mill's aeration stabilization basin has been shown to be contaminated

with 2,3,7,8-TCDD at 210-350 ppt (Beak 1989). However, it was not expected that the PCDDs and PCDFs would escape from the site. Firstly, PCDDs and PCDFs were not detected in leachate samples from either the Miscampbell site or the Ski-Hill site (OMOE unpublished data). Secondly PCDDs and PCDFs are not likely to be found dissolved in water. A standard measurement of a compounds tendency to remain dissolved in the water column as opposed to other compartments in the environment is the octanol/water partition coefficient (K_{ow}) which is the ratio of the proportion of a compound that will partition into octanol to the proportion that will partition in water. The higher the K_{ow} the less likely the compound is to dissolve in water. Since the $Log_{10}K_{ow}$ of PCDDs vary from about 6.6 to 8.2 (Shiu *et al.* 1988) this group of compounds should sorb to particles and, based on this property, Murphy (1989) modelled the migration of TCDD from incinerator ash in landfills through aquifer soils. He concluded that this and other PCDD congeners should not escape through groundwater from a site if properly designed and maintained.

The above information suggests that the loss of PCDDs from both wood waste disposal sites has been through the direct erosion of material only and not through groundwater movement. An inspection of the Ski-Hill site which showed that wood-waste material was being eroded from the site, supports this hypothesis. In addition, the proximity of the drainage ditch to the Ski-Hill site would facilitate the direct transport of leachate into Frog Creek. No inspection of the Miscampbell site was made.

The source of the tetraCDD found in mussels from the agricultural drain is unknown. It

does not receive drainage from any of the wood waste disposal sites and there do not appear to be any other sources in this watershed.

The Use of Mussels For Biomonitoring

Since PCDDs were found in mussels in Frog Creek at the confluence of the Ski-hill drainage ditch, but not upstream, we concluded that the highest concentrations in water were in the Ski-Hill drainage ditch. However, PCDDs were not detected in mussels exposed in the ditch. This has important implications for biomonitoring studies because it contradicts the basic assumption that there is a relationship between ambient levels of a contaminant and the levels found in the biomonitoring organism.

The reason that PCDDs and PCDFs in mussels were not detected in the Ski-hill drain is likely due to the interaction of three factors: the hydrophobic nature of PCDDs; the feeding/respiration behaviour of mussels; and water quality conditions in the ditch.
In general, the more hydrophobic a compound (as measured by its K_{ow}), the longer the time required to achieve equilibrium in biological tissue, and also the more important food becomes as a route of uptake. PCDDs have high K_{ow}s and consequently require long periods to achieve equilibrium in biological tissue.

The gills of mussels are adapted to both respiration and feeding, with both processes occurring simultaneously (Barnes 1963). One of the benefits of using mussels as biomonitors is that many chlorinated organic contaminants (e.g. PCBs, HCB) approach

equilibrium in their tissues in a relatively short period of time, often less than 21 days (Olive and Waller 1989). This is likely the result of passing large volumes of water over their gills to extract food during which time contaminants will be absorbed through the gills.

Water quality can indirectly affect the rate of uptake of contaminants. When conditions are unsuitable, for example, during sediment resuspension episodes mussels are known to close up and cease feeding until the waters clear, except for short periods to respire. Such behaviour would inhibit the uptake or elimination of contaminants during the episode (Olive and Waller 1989) and so, should increase the length of time to achieve equilibrium with the environment. For compounds that require a relatively short period to approach equilibrium, a reduction in filtering rate may not have a significant effect on final tissue levels because brief periods of respiration may be adequate to achieve equilibrium even during an exposure period as short as 21 days. In the extreme, that is, for compounds having very high K_{ow}s, and for conditions that would prevent mussels from filtering, except for short respiratory periods, non-detectable levels of the compound might be expected in mussel tissue.

This study has demonstrated that, under certain conditions there can be a violation of the basic assumption of biomonitoring studies. The assumption is that there is a relationship between ambient levels of a contaminant and the levels found in biomonitoring organisms. As a general rule, for source identification biomonitoring organisms should be placed as close as possible to suspected sources. This rule should be relaxed when the following conditions apply: the compound of interest has a high K_{ow}; the character of the effluent or

visual evidence suggests that conditions will be stressful to mussels.

CONCLUSIONS

1. The Ski-Hill wood waste disposal site was identified as the major source of PCDDs to Frog Creek. PCDDs which were found previously in the mill's lagoon sludge are likely being mobilized through erosion at the wood waste disposal site and appear to be entering Frog Creek via a drainage ditch.

2. The Miscampbell wood waste disposal site was identified as a minor source of PCDDs through the Gun Club Creek to Frog Creek.

3. There was no evidence that PCDDs from the new wood waste disposal site are entering Frog Creek.

4. Low levels of tetraCDD were found in mussels from an agricultural drain. The source of the contamination is not known.

5. Mussels exposed in the drainage ditch did not accumulate detectable levels of PCDDs because of the high K_{ow} of PCDDs and suspected poor water quality conditions in the drainage ditch which inhibited uptake by mussels.

RECOMMENDATIONS

1. Remedial measures should be undertaken at the Ski-Hill site to ensure that no further erosion of wood waste material occurs and leachate short-circuiting via the drainage ditch is controlled.

2. The Miscampbell Site should be inspected to determine where material is eroding from the site and the necessary remedial measures taken.

3. The drainage area of the agricultural drain should be inspected to determine the source of tetraCDD.

4. Measures should be taken to ensure that contaminated drainage from the new wood waste disposal site is controlled.

5. When the measures outlined in 1. to 4. above have been completed, a biomonitoring study should be undertaken to assess PCDD levels in Frog Creek.

6. Both adult and young fish should be analyzed from Frog Creek and Stanjikoming Bay to determine PCDD and PCDF body burdens related to the human consumption of fish.

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